

Paper submitted to Department of Defence Explosive safety Seminar held at Las Vegas USA on 20 - 22 August '96

THE NITROGLYCERINE - THE SAGA IN INDIA WE STILL NEED FOSTERING IT (?)

1. Introduction

Nitroglycerine is well identified with the code letters NG in the propellants and explosives circle. Even after handling exactly one and a half century since its discovery by Ascanis Sobero in 1846, pronouncing the letters NG, even now gives Nitroglycerine a place of pride and a feeling of obscurity thrill, and untouchability. Nitro glycerine a highly sensitive explosive in liquid form denied its use for about a quarter of century till the ever remembered great human being Sir Alferd Nobel put that in the usable form of Dynamite in 1867.

NG is one among the largely produced explosives such as Nitro Cellulose, Ammonium Nitrate and TNT (Tri Nitro Toluene). The Nitro Cellulose has become comfortably handled explosives/non-explosive. Ammonium Nitrate turned a handy explosive cum Fertiliser. The TNT sounds as a chemical rather than explosive. But NG even now demands a lot of attention and caution in its manufacture.

NG has never allowed its transport naked and evades even now carrying over long distances even in its administered forms such as absorbed in Kieselgurh or dissolved in solvents (not ordinarily seen) due to its high sensitivity, to friction and impact. Due to its chemical and explosive hazards or simply due to its problems in handling, it is being slowly phased out especially in mining activities. However its use in propellants still continues and its manufacture and handling has to continue inspite of its hazards.

A number of improvements(?) in the process and changes in technologies have been adopted over the years, to improve the safety. Even now causes are not eliminated altogether and accidents do occur with loss of life, causing concern for the producer and the humanity. When we are still to produce and use it inspite of its processsing hazards, the right direction towards safety is to make the effects of the accidents insignificant. Bulk handling of NG can be stopped and its in situ consumption can be a solution in this direction. In other words, we can nurture and foster the NG only to a child and dont leave him grow any more to turn ultimately ugly.

2. Uses over the period

NG production started in India some where around 1905 for use in the manufacturing "Cordite" the Nitro Cellulose (NC) - Nitro Glycerine double base propellants for small arms and Gun ammunition by the then British Colonial Government. Its use remained exclusively in the manufacture of propellants as a liquid explosive gelatiniser for the insoluble solid high nitrogen Nitro Cellulose (called gun cotton) facilitating the use of both in the 'Noble' way removing their individual identity and ferociousness. In sixties, in the post independance era its use in the mining sector in the form of Blasting Gelatine or Ammonium Nitrate Gelatine mixture started and the consumption increased manifold over the years out weighing its use in propellants. Use of NG in the rocket propellant also did come up a little later and remained buoyant till other liquid propellants came up. The present trend is to withdraw it in the commercial mining due to its hazards but in the field of propellant manufacture the use continues.

3. Technologies adopted over the period.

Over the period since the NG came into being in India, the Batch process remained for about

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7 decades upto 1970 and then came the improved continuous process units. Among them are the Nilssen And Brunnberg (NAB) process developed in Nitro Noble Aktie Bolagat Sweden adopting injector nitration, dynamic separation of emulsion, pipe line washing etc. The more automated and remote controlled plant versions in this technology incorporating improved washing methods also came later. Other technology came in the year 1975 include Mario Biazzi Sweden method which adapts high speed emulsification nitration and washings and static separations in contrast to the NAB process. Latest version of Joseph Messener's insitu mixing of sulphuric and nitric acids to prepare nitrating acids and nitration using injector methods has also come up.

4. Changes adopted towards improvement in Safety.

A good number of changes and modification have been incorporated in the continuous plants of different technologies, each having its own comparative advantages and disadvantages. The changes include the process changes, improvement in the unit operations, reduction with explosive holding and in NG handling methods. A few which have bearing on the improved safety are given.

4.1 Changes in the process:

4.1.1 The old batch process was changed to continuous process with a number of advantages. This has changed the need for large bulk handling of unstable acidic NG and manual operations demanding exacting precision, control and care in operations, and maintenance of equipments. It has given sense of relief from a tense atmosphere to a fairly easy and comfortable situation for both the process operators as well as the Managers.

4.1.2 The continuous plants are either automatic with limited manual controls or remote controlled. The need to expose personnel to hazards has been by and large removed in the plants. But in NG intermediate Storage Buildings limited exposure and risk is always there.

4.1.3 The continuous plants have enabled large turn out in production with limited fatigue to the operators. The operator excessive dependance and susceptibility to commit mistakes due to pressure has been over come.

4.2 Changes in unit operations:

Nitration:

4.2.1 There is an excellent improvement in this operation in the continuous process over the batch process. In the batch process, the Glycerine is sprayed with compressed air to the bulk of the nitrating acid agitated by air and cooled by chilled water coils to take away the heat of reaction and temperature is controlled. Theoretically the ratio of nitrating acid to glycerine can be considered as varying from infinity in the beginning to the fixed value of about 5:1 at the end of addition of glycerine. The initial addition of glycerine has always its attendant risk of undesirable oxidation and decomposition reactions which can go uncontrolled. In the NAB process the glycerine and air mixture is sucked by the jet of nitrating acid and the ratio changes is only for a few seconds of the nitration starting. Then the ratio remains constant. In the Biazzi process, the addition of mixed acid and glycerine are synchronised and there is no variation in the ratio. In both the process, the mixing of glycerine and acid are fast, efficient and almost instantaneously the nitration is completed and emulsification occurs. Occasionally in the Biazzi plant the NG and Acid emulsification become so strong that separation does not proceed easily in the separators with the risk of carrying acid to the washers and consequent effects.

4.2.2 Separation of NG and waste acid (or refuse acid or spent acid after nitration)

This is the most critical accident prone area in the whole of NG manufacture. A number of accidents in NG plants all over the world would have occurred in this segment of production. In the

batch process, when nitration is completed, the NG-waste acid emulsion is rundown to the square shaped lead tank. Once the separation of the NG is complete as can be seen by the formation of a clear line between the two phases, the NG is run down through upper cock to the washing tank and the acid is rundown through the bottom cock. The un-separated emulsion is either drawn alongwith NG or to the drowning tank depending on the situation. In this process of separation, due to presence of sludge (mostly sulphates of metals), the separation time varies. For better separation a longer time is allowed even after separation has occurred. Some time the third non-reactive liquid such as liquid paraffin is added to enhance separation. A large quantity of acidic NG which has low stability is handled in this operation demanding intensive care surcharged with tension. Occasionally decomposition reaction can set in and the whole charge has to be drowned to large amount of water.

In the remote controlled continuous Biazzi plant an oval shaped highly polished steel, semi static separator is employed for continuous receipt of emulsion and separation. The NG/Acid emulsion which has acquired a large momentum due to high speed stirring in the nitrator enters horizontally into the middle of the separator where the cross section area is highest gets gradually separated the two phases. The heavier acid layer going to the bottom is continuously drown out through automatically controlled valves which opens or closes depending on the level of the acid/emulsion in the separator. The NG separated to the upper portion freely overflows through a funnel to the washers. Two accidents in NG plant occurred in this separator in India detonating the whole plant luckily with no human casualty. The causes may be due to the decomposition of acidic NG pockets staying on the surface for longer duration, or due to the impurities accumulated on the surface during decomposition of NG etc.

In the NAB process, the separation of NG/Acid emulsion is done using an Alfa Laval Centrifuge employing the differential specific gravities of the two liquids. The quantity of NG held in this centrifuge is hardly a kg partly as separated NG and partly in the emulsion form. Centrifuge is erected in a cubicle protected with the Blast walls that the blast effect is insignificant. There is another safety arrangement provided that as and when the centrifuge RPM reduces below certain level, the spent acid removed for denitration is stopped. This ensures free NG or emulsified NG escapes alongwith spent acid sent for denitration. The Biazzi's latest plant have changed over from static separation to centrifugal separation.

4.2.3. Washing of NG produced:

Various techniques are adopted to wash away the traces of acid carried by NG in the NG/Acid separation. The oldest methods is to take the acidic NG over water or soda solution and give agitation with air using air coils controlling the temperature rise due to dilution/ neutralisation by chilled water circulation. In the ICI's NAB process, the separated NG from the centrifuge is drawn to a small bowl and educted with a jet of hot water in a 20 mm dia pipeline which emulsifies the NG. Air is also injected to it for further emulsification. The acidity is then removed effectively in this process and the NG/Water emulsion is separated using a centrifuge. The NG is further washed with soda solution. The NG held is about 5 kg in the line in form of emulsion.

In the Biazzi process, the acidic NG is drawn into washers, neutralised with 12% soda solution and agitated with stirrers. The PH of the solution is controlled by the addition of required quantity of soda solution. The NG is separated from the emulsion by static separation and washed further with cold water. The washing in this way has been very effective but the NG quantities held are high compared to the NAB process. In other plants column washings as well as use of Norrel separators are adopted.

Though the NG coming out of these plants are suppose to be passing the test for stability and other parameters, often then not, the NG fails for stability and additional washings using any of the washing methods are to be employed to improve the quality.

4.2.4 Collection of samples of NG:

In the old process, a small quantity of 1 to 2 kg is drawn into the filtration vessels from which a few ml of NG is drawn through the outlet to Aluminium containers. In some plants the separated NG is pipetted out using suction created by water jets and transferred to glass containers. In some systems, the NG/water emulsion itself is sampled by pipetting and the NG is allowed to separate. The sampling technique assumed importance owing to an accident in one of the NG storage and washing house, attributed to dropping of the samples.

4.3 NG handling methods.

NG due to its frictional sensitivity is not subjected to mechanical driving. It is always educted with water. In the old batch process, the NG is run in the lead gutters/pipes from one process building to other. Later in the continuous plants it is educted with high pressure water jet and carried in high density polythene pipes in the form of emulsion.

Different dimension of the pipes as well as the different ratios of the NG:water emulsion ranging from 1:0.75 to 1:3 times are employed in different plants considering the economy. Such emulsified NG when passed through pipes whose dia is less than the critical detonation diameters of the respective emulsions render the transport of NG in between process buildings safe. In old batch process units, NG is kept in storage till its clearance or consumption in the naked form under mild alkaline solutions. Entire quantities of NG produced is consumed by the end of day in the cold places to avoid freezing of NG (at 13 degree C) and its consequent hazards due to its crystal-crystal friction. In hot tropical places, NG is held over night in the naked form or in the NG-water emulsified forms considering it more safer.

4.4 Explosive holding reduction:

The remarkable improvement of the continuous process over the batch process is the reduction in the explosive holdings. In a batch process, the NG holding with plant has to be at least the same as the batch size of say 500 kg or 2 to 3 times the batch size depending on the cycle time given in the different operation. This has been slashed to a meagre 50 kg in NAB process plant of capacity 680 kg/hour which work out to only 7 to 8% of capacity. In a similar capacity Biazzi plant, the holding works out to 280 kg which come to 40 to 45% of its capacity. In the Joseph Missners new plant the holding in all is a little more than the value at 350 kg/hour i.e. 50%. Further to the reduction in the holdings, in the continuous plants the NG holding is mostly in the form of NG/Acid or NG/Water or NG Soda emulsion which considered more safer than naked or acidic NG making the continuous process more safer and less potential.

5. A few major accidents in NG production causes and lessons.

In India three major accidents took place in the NG production units alone one each in each decade of seventies, eighties and ninties which has caused enormous strain in the minds of the plant personnel and the managers. As brought out in the Biazzi's publication 'Accidents' by Biaguti, the two accidents one in 1975 and the next same day/date/month in 1985 in the Biazzi plant of the same site due to decomposition/detonation of acidic NG in the NG/Acid separator. Though the whole plant has blown off on both the incidents, there was no human casualty as the plant was a remote controlled. In the third accident in 1992, one of the NG storage cum washing house of the NG plant was blown off. There was 6 human casualties which included a death due to missile flying from the site fatally knocking an innocent worker who was taking tea in a distant shed.

This accident an unprecedented in the NG manufacture in India in a fairly considering safe place in an unpredictable way was intriguing and draw the attention in a large way. Various considerations to avoid repetition of such an accident is underway. But most important one is to consider now to avoid exposure of the personnel to the potential risks.

6. Improvement in technology; Has it reduced the accidents? Human aspects.

As been discussed in the earlier paras, there has been a marked improvement in the technology, processing and handling methods incorporating lot of safety in the present continuous plants over the batch process. However, in India, where one of the oldest batch process NG plant was operated in the first seven decades of this century without any serious mishaps, there were 3 accidents in the last 3 decades. Can we attribute this to the less stringent work ethics of operators compared to the sacro sanct practices of the earlier decades due to the environmental charges and increased stresses on the human being now a days?

7. Is it time we eliminate handling NG altogether.

Inspite of the marked improvements as we have seen there are number of accidents occurring even now. In the NG consuming industries, either in the propellant factories or in the dynamite producing factories, at some stage NG is held bulk upto 1 or 2 tonnes which is always a potential risk. Instead of keeping the potential risk and try to eliminate personnel from exposure can we try and eliminate the potential risk itself. We can avoid keeping NG in bulk at any cost and risk. In the case of propellant manufacturing units, the NG coming out of continuous NG plant can be mixed with nitro-cellulose to obtain the right NC-NG paste slurry which is not hazardous as NG itself. Similarly in the NG - mining explosive producing factories, the NG is continuously poured to the continuously moving other components and NG is absorbed as and when produced. By this techniques as we have come out from the batch process holding large quantity of NG to less potential continuous plants, we can remove the potential NG storage units. This will go a long way in saving human being subjected to risk.

8. We need NG production for now and probably for some more decades from now. We still need to consider NG an alien and a child we can see him only as a child looking pretty but don't allow him to grow and turn ugly.

Concluded.

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